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# Tyurin's Method and Other Methods Used in Understanding Humification and Aggregate Formation

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This study first gives an overview of the nature of the components which comprise soil organic matter. Tyurin's method of humus fractionation is then compared to other methods which radically break down aggregates (Bruckert and Gaiffe method). The results of this comparison provide useful information as to the role of three cations (calcium, iron, and aluminum) in humification. Two experiments conducted by one of the authors show the importance of soluble calcium in the formation of both microaggregates and macroaggregates. The authors investigate the action of iron and aluminum hydroxide, the makeup of the various humic compound forms, and the biomolecules which act as the "cement" in binding both microaggregates and macroaggregates. Conclusions are drawn as to the three processes involved in humification, structuring and pedogenesis which are conditioned both by the climate and cations freed by weathering. The main processes are further defined: podzolization, brunification, andosolization, calcic and climatic melanization.

**Key words:** Fulvic acids, humic acids, humin, biomolecules, humification, humus form, mor, mull, podzols, brown soil, rendzina, humo-calcic soil, andosol, chernozem

## 1. Introduction

Modern-day soil scientists agree on the important role played by organic matter in pedogenesis. Its effects can be seen when studying soil with natural vegetation, such as forestland or steppe. Fresh litter is transformed both through the processes of mineralization and humification. During humification, new molecules, humic and nonhumic compounds are formed, which are mineralized as well, though more slowly than fresh litter.

**Nonhumic compounds** have two types of components: (1) Plant residues which are only partly transformed and (2) biomolecules (polysaccharides, proteins and lipids) which result mainly from microbial activity.

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Fractionation of Humic Compounds (HC) of Three Soils

| Soils | Total Org. C, % | C % of total C | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | | Plant resi-dues | Non-extr. fraction | Extractable fraction | | | |
| | | | | HC 5 | HC 10 | HC 12 | Total |
| Humo-calcic | 19.3 | 35.7 | 18.2 | 12.8 | 22.2 | 11.1 | 46.1 |
| Brown | 3.8 | 23.6 | 13.5 | 30.2 | 17.5 | 15.2 | 62.9 |
| Chernozem | 3.7 | 5.7 | 14.0 | 3.7 | 55.9 | 20.7 | 80.3 |

**Humic compounds** are formed by a process called neoformation. The litter's components decompose into simple particles which form new humic compounds. The phenolic (or quinonic) constituents comprise the "round nucleus" and the aliphatic ones make up the "side chains." Both fractions are of different importance depending on the kind of humic compounds and humus formed.

Neoformation is the main process in the humification of various forms of biologically active humus, namely mull. This form of humus is characterized by the rapid decomposition of fresh litter and the formation of aggregates of clay-humus complexes. In the humus called mor (*Rohhumus*), which is only slightly active, litter decomposes slowly and only partially to form a thick, fibrous cover over the mineral soil in which no aggregates are formed. In fact, biologically active humus (that is, mull) show great morphological variations in the organomineral horizon depending on the environmental conditions.

Tyurin (1937, 1951) emphasizes the importance of free cations in the formation of organomineral complexes. He developed a progressive method for extracting the humic fractions by releasing first the weaker organomineral bonds, then the stronger ones. Numerous other progressive methods were later developed. Bruckert and Gaiffe worked out a method based on the radical breakdown of all aggregates in soil (1983). Comparison of these two methods aids in a better understanding of the role of the cations, Ca, Fe, Al in aggregate formation.

## 2. Methods of Humic Compound Extraction

Tyurin's method (1940, 1951), modified by Kononova (1961), separates the soil into two types of fulvic acids (FA) and three sorts of humic acids (HA):

- Fraction 1: Free HA and HA bonded to the mobile forms of sesquioxides
- Fraction 2: HA bonded to $Ca^{2+}$
- Fraction 3: HA bonded to stable iron and aluminum hydrates

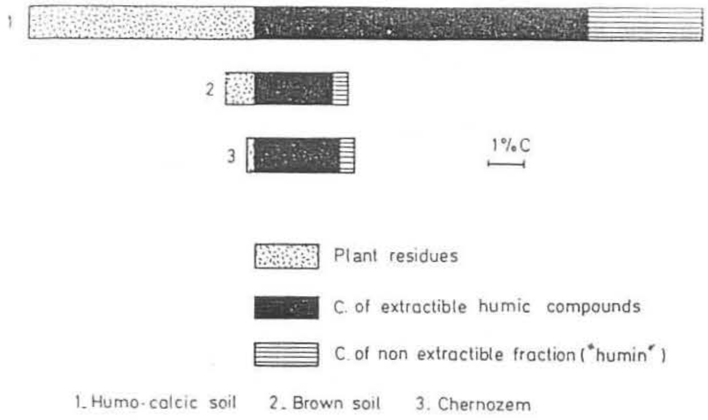

Fig. 1. Repartition of carbon between the three forms.

The different extraction methods used in France make use of more and more complexing reagents at an increasingly higher pH level (after eliminating plant residues). Sodium tetraborate buffer at pH 9.7, pyrophosphate Na at pH 9.7, pyrophosphate NaOH at pH 12 (Bruckert and Metche, 1972).

All of these methods, however, present a major drawback in that they cannot disperse the strongest aggregates, especially those which are strongly bonded to minerals, so that the humic compounds only partly dissolve. The ratio of extractable organic matter (CFA + CHA/TOTAL C) then becomes abnormally low, as there is a large amount of humin. For this reason, Bruckert and Gaiffe developed a method which breaks down all aggregates immediately and completely before using complexing reagents. For calcium-rich soils, the extraction ratio is much higher than with progressive methods (50–70 percent for humo-calcic soil, 80 percent for a chernozem).

### 2.1. Method

This method is described in detail by Bruckert and Gaiffe (1983) and is only summarized here in note form: each type of treatment is symbolized by a letter followed by a digit when the treatment is repeated several times.

(1) Elimination of binding cations at pH 5 (HC 5 fraction)

$H_1$ : Decarbonation with diluted HCl (pH 2–3)
$D_1D_2D_3$ : Extraction with heated dithionite Na (+NaCl) (repeated three times)
Na : Rinsing with NaCl
$H_2$ : HCl 0.1 N treatment

(2) Extraction at pH 10 (HC 10 fraction)

$P_1P_2P_3$ : Extraction with pyrophosphate Na, 0.1 N (with flocculation of clay with KCl) (repeated three times)

Sifting to 50 μm

(4) Extraction at pH 12 (HC 12 fraction)

$P_1P_2P_3$ : Extraction with pyrophosphate Na, 0.1 N + NaOH 0.1 N (repeated three times)

### 2.2. Materials

The following three Ah horizons were used:

- Humo-calcic soil: pH 7, C percent: 9.3 located at Lerrieux (Jura), altitude: 1300 m
- Brown soil: pH 5, C percent: 3.8 located at Laveron (Jura), altitude: 900 m
- Chernozem: pH 7, C percent: 3.7 located in Ukraine, altitude: 320 m

### 2.3. Results

The table and Fig. 1 illustrate significant differences in the three soils. The extraction ratio of humic carbon (extractable C/total C%) is much higher in chernozem than in humo-calcic soil, the ratio in brown soil being found between the two. The remaining plant tissues (larger than 50 μm) show the inverse trend, indicating that the extent of humification increases progressively from humo-calcic soils to chernozems. The nonextractable fraction is insignificant in all three soils. Furthermore, this fraction still contains a large amount of very fine plant residues which can be observed under microscope. This method thus greatly reduces the actual "humin,"

The distribution of extractable carbon highly varies for each of these soils: in brown soil, nearly half of the extractable carbon is included in the HC 5 fraction (HCl and dithionite), indicating the weak bonds of these humic compounds with iron. However, this fraction is found only in small amounts in humo-calcic soil, especially in the chernozems, which means that the bonds bonding humic compounds with iron (and aluminum) in these soils are stronger and can only be broken by pyrophosphate. This observation is confirmed by the successive extraction of cations shown in Fig. 2. Whereas calcium which is found in its highest amounts in humo-calcic soil and chernozems is entirely removed by the first extraction (HC5), iron is only partially extracted, and aluminum is not extracted at all, as they can only be extracted by pyrophosphate.

### 2.4. Discussion of Methods

Comparison of the different methods for extracting humic compounds indicates the role of cations in humification.

The importance of calcium in both its exchangeable and complexed forms (Blonde, 1989; Valles et al., 1989) is clearly demonstrated in both methods. Tyurin's method shows the importance of fraction 2 (HA) in chernozems. The Bruckert-Gaiffe method breaks down all calcic aggregates by initially strong acidification. Iron, however, appears to be somewhat more complex. In acidic brown soil, the weak organometallic bonds are broken just as easily by NaOH (Tyurin's

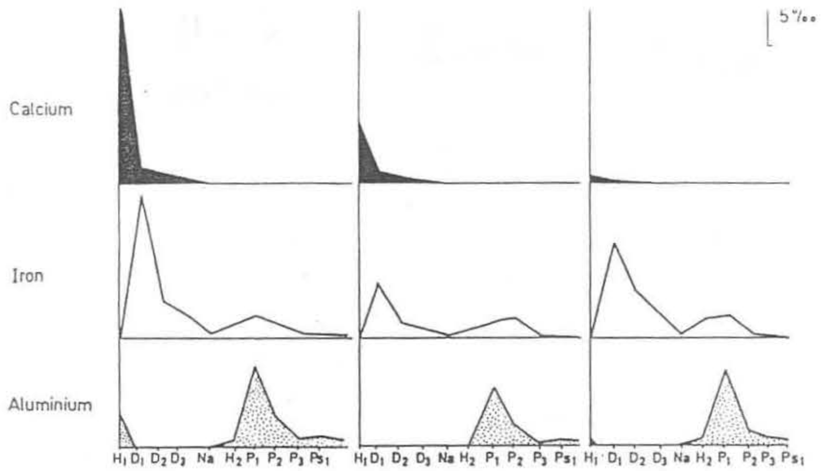

Fig. 2. Extraction mode of cations by successive reagents.

fraction 1 HA) as by HCl-dithionite (Bruckert-Gaiffe method). However, a part of the iron and almost all of the aluminium have much stronger bonds which can only be broken by the strong reagents like those of Tyurin's fraction 3 (HA) or the pyrophosphate used after strong acidification and reduction in the Bruckert-Gaiffe method.

These conclusions lead to further investigations as to the way these three cations, Ca, Fe, Al are bonded.

## 3. The Role of Cations in Aggregate Formation

The various humus fractionation methods studied have revealed significant differences between the action of calcium and iron and aluminum hydroxides.

### 3.1. Calcium

This cation plays a key role in extremely humic soils formed on limestone (for example, rendzina), and in humo-calcic soils in the mountains. To demonstrate the importance of calcium, two experiments were conducted in the Ah horizon of humo-calcic soil. These experiments—described in detail by Gaiffe (1987)—are only summarized here.

**Experiment 1.** Aggregates were mechanically agitated in water with glass beads, then sifted to 50 µm, producing fractions with two different-sized particles: 65 percent particles > 50 µm; 35 percent particles < 50 µm. The fraction made up of particles larger than 50 µm was chemically treated and analysed. The portion contained only 15 percent plant residues and 50 percent clay after elimination of the organic matter with $H_2O_2$. These results indicate that this fraction is mainly composed of large-sized aggregates, called macroaggregates. Comparison with the brown soil showed that this type of soil is made up of 18 percent stable aggregates larger than 50 µm containing 10 percent plant residues.

**Experiment 2.** The purpose of this experiment was to demonstrate that the fraction of particles larger than 50 µm was composed of smaller-sized aggregates which were also stabilized by calcium (that is, microaggregates). This fraction was incubated for 27 weeks at 25 °C with periodic leaching using a solution of KCl to replace the $Ca^{2+}$ by $K^+$ in the absorbing complex, as $K^+$ does not have the stabilizing effect of calcium. The $Ca^{2+}$ decreased from 60 meq/100 g to 10 meq/100 g in the complex (Fig. 3). A decrease in organic matter content due to mineralization was observed at the end of the experiment. Moreover, the stability of the aggregates agitated in water was reduced considerably. Only 20 percent of the clay fraction was dispersed before incubation compared to 60 percent afterwards; this is approximately the same amount obtained with textural analysis (increased by the nondestroyed plant residues).

The results of both experiments obviously show that the humo-calcic soil, like humic rendzina, is made up of macroaggregates which are formed by the clustering of microaggregates. Calcium is an effective stabilizing agent for both macro- and microaggregates.

### 3.2. Iron and aluminum hydroxides

Iron and aluminum are complexed by soluble organic matter which becomes insoluble when the proportion of metal to organic matter is sufficiently high (Tyurin, 1940). Two types of complexes have been described by various authors (Nguyen Kha, 1973; Theng and Scharpenseel, 1975; Senesi et al., 1985). The first complex is an unstable type, M–OH–HA (or M–OH–FA) in which iron or aluminum retains its cationic properties. In this type of complex, metal serves as the binding cation between clay and organic matter. It corresponds to the fraction 1 of HA in Tyurin's method. In the Bruckert-Gaiffe method, this complex is broken down by the combination of HCl-dithionite. This type of complex is the dominant form found in Atlantic brown soils.

The second type of complex, which authors refer to as a "quadridentate," meaning "with internal sphere," involves 4 parts oxygens; metal loses its cationic properties. This type of complex seems to correspond to Tyurin's fraction 3 (HA). In Bruckert and Gaiffe's radical method, this complex can only be destroyed by pyrophosphate (Fig. 2). It is typical of melanized (that is, black) forms of humus, like some rendzina, humo-calcic soils, and chernozems. In these soils, the three cations, Ca, Fe, and Al, mutually strengthen themselves. However, in the melanized andosols of Japan, aluminum and iron act alone, even in very acidic environments.

Hence, in calcium-rich environments, calcium aids in the formation of macroaggregates which are complexed by the clustering of microaggregates. In acidic environments, complexed iron and aluminum form a bond between clay and organic matter, as in brown soils. However, in some acidic ashy volcanic material, aluminum, and iron can also replace calcium in building stable humic compounds (Hetier et al., 1975). When there are not a sufficient number of cations, the soluble organic matter remains mobile and furthers the process of podzolization.

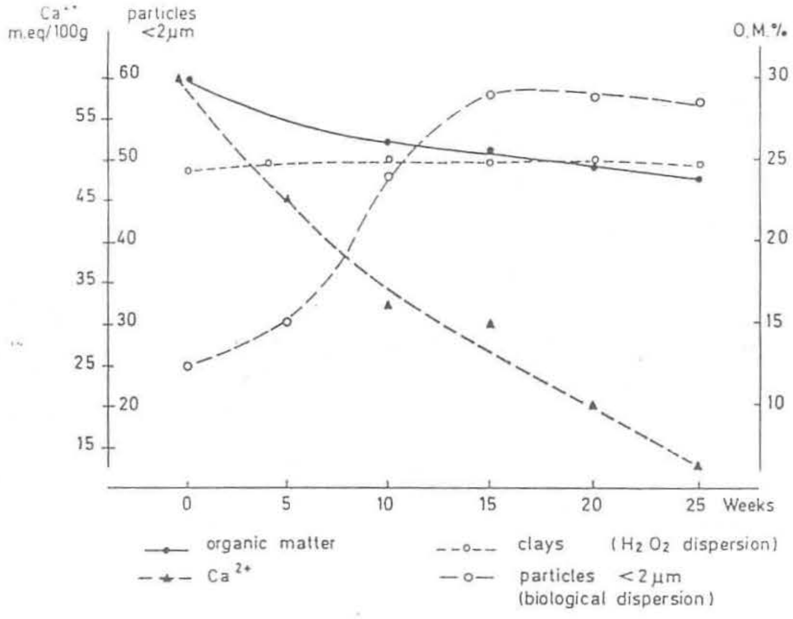

Fig. 3. Incubation of humo-calcic soil with periodic KCl treatment: evolution of OM, clay, saturation by calcium.

### 4. Nature and Composition of Humic Compounds Occurring in Soil Aggregates

The process of humic compound transformation can, according to Andreux (1975), be summarized as "the elimination of the aliphatic chains, which increases the hydrophobicity of humic macromolecules and lowers their solubility, the more polycondensation there is. Humin, according to Tyurin (1951) and Preston et al. (1989) is comprised of humic compounds which are strongly bonded to minerals and can no longer be extracted by reagents. According to several authors (Tyurin, 1951; Flaig et al., 1975; Ponomareva and Plotnikova, 1977; Orlov, 1974), the major humic compounds can be classified as follows:

- Fulvic acids (FA): these are divided by Tyurin into free and mobile forms (fraction 1A) and the forms which are strongly bonded to humic acids, fraction 1).
- Humic acids (HA): these are of two types: brown humic acids (Tyurin's fraction 1) and gray (or black) humic acids (Tyurin's fractions 2 and 3). The first type is less condensed and more aliphatic than the second. With wet and dry seasons, brown humic acids are transformed into gray humic acids by increasing the nucleus size and by splitting the side chains. They become more and more resistant to biodegradation (Alexandrova and Nazakova, 1977; Mal et al., 1982; Baranovskaia et al., 1984). This process is generally referred to as maturation.

Authors use a battery of tests to observe this transformation; these tests are briefly discussed below.

- Aromaticity: during the transformation and aging of humic compounds, aromaticity increases and aliphaticity decreases, as demonstrated by Orlov et al. (1987) and Schnitzer et al. (1991).
- Atomic H/C ratio of humic acids: this greater than 1 for brown HA and lower than 1 for gray HA.
- Optical density: E4/E6 is lower for gray than for brown HA.
- Hydrolysis HCl6N: this destroys the aliphatic chains but preserves the aromatic nucleus relatively well, especially the "humic nitrogen" inside the nucleus.
- Mean resident time (MRT): this represents humic compound resistance to biodegradation. MRT decreases as the turnover increases. According to Scharpenseel (1972), Rubilin and Zozyreva (1980). Cherninski (1986), brown HA has a much lower MRT (and a much faster turnover) than gray HA.

The main factors in the extent of humus maturation are climate and biological activity. For instance, in the area once forming the USSR, humus forms in soils can be distinguished successfully from north to south as mor, forest mull, and chernozemic mull, respectively. These forms are characterized by the greater extent of humification and maturation (Kononova, 1984). Mor is only slightly humified, as plant residues are not completely transformed. Forest mull is moderately mature, the stage of brown HA being not overreached. Chernozem mull is the most fully transformed, and the abundance of gray humic acids give it a black color (melanization). This stage of maturation is not found in the Atlantic brown soils due to the climate which lacks sufficient variation. Alternating periods of wetness and dryness are crucial for melanization to take place. According to Orlov et al. (1987), the irrigated chernozems are more aromatic than their nonirrigated counterparts due to the alternating wet and dry cycles.

Calcic mull of humic rendzina, and particularly humo-calcic soils occurring in limy mountainous areas, or in some subboreal plains (Schaetzl, 1991) show a kind of humification which shares some of the characteristics of brown soil (for example, high FA/HA ratio) and some of chernozem (high gray humic acid content).

## 5. Biomolecules and Their Role in Aggregate Formation

Several authors have pointed out the essential role of biomolecules, especially in polysaccharides, in forming aggregates (Chassin, 1979; Faivre, 1984; Chenu, 1989; Jocteur-Monrozier and Duchaufour, 1986; Jocteur-Monrozier et al., 1991). Nitrogen and calcium-rich environments favor the synthesis of biomolecules by combining the action of both microorganisms and earthworms, resulting in the formation of large aggregates. The abovementioned experiments show that these large aggregates go through two phases: microaggregates which cluster to form macroaggre-

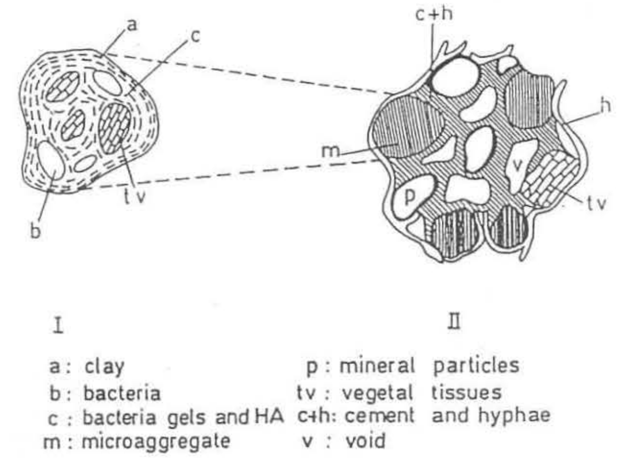

Fig. 4. Microaggregate and macroaggregate.

gates. According to a number of authors, the cement binding microaggregates is made up of bacterial gels and HA, whereas fibrous polysaccharides and hyphae bond these microaggregates together to form macroaggregates (Tisdall and Oades, 1982; Oades, 1986; Bruckert and Gaiffe, 1983; Bartoli et al., 1988; Shipitalo and Protz, 1989—Fig. 4).

The turnover of biomolecules which form the cement of microaggregates is much slower than that of macroaggregates, which are periodically destroyed and rebuilt. Several authors have pointed out the special stability of calcic microaggregates (Lichko et al., 1984; Tiessen and Stewart, 1986; Gupta and Germida, 1988).

Microbial gels are strongly bonded to gray humic acids and adhere well to the surface of clay particles (Chassin, 1979; Barriuso, 1985). Both are extracted by pyrophosphate at pH 12 (Blonde, 1989). Large aggregates depend on biological activity and on pedoclimatic seasonal changes.

**Mor.** Mor found in boreal and Atlantic podzols shows very slight biological activity due to its acidity and high antimicrobial compound content. These conditions are aversive to biomolecule formation, and, consequently, true aggregates cannot form.

**Forest mull.** Forest mull found in Atlantic brown soil and many dernovo-podzolic soils contains only 15 to 20 percent biomolecules (Barriuso 1985). According to Jocteur-Monrozier et al. (1991), forest mull microaggregates contain more plant residues than biomolecules, which decreases their stability.

**Chernozemic mull and calcic mull of rendzina** are the only humous forms which have all the best-suited conditions for the formation of highly stable microaggregates and macroaggregates.

## 6. Conclusion: Humification, Aggregate Formation, and Pedogenesis

Tyurin's method, updated by more recent information, provides a better understanding of the processes of humification, aggregate formation and, consequently, pedogenesis. This is confirmed by the observations made in the succession of soils in the area once forming the USSR from the north to the south: podzols, boreal leached soils, chernozems (Kononova, 1984).

The humous form, whether mor, forest mull, or chernozemic mull, depends on environmental conditions such as climate, pedoclimate, parent material, and vegetation. Two factors are especially influential: (1) climate, which must be seasonally varied, and (2) nature and amount of cations released by weathering.

Depending on these factors, humification and pedogenesis may be characterized in the following three ways: (1) lasting persistence of soluble organic compounds (that is, podzols), (2) insolubilization of these compounds, followed by moderate maturation resulting in brown HA, and (3) strong polycondensation producing gray (black) HA, through the process of melanization.

These three manifestations of pedogenesis correspond to three different climates:

(1) Cold climate, shown by the presence of mor; very few cations are released by weathering. Free fulvic acids favor the complexation and leaching of mobile organomineral complexes which characterize podzolization. In Atlantic humic climates, this process occurs only in sandy material and under heath.

(2) Temperate humid climate, that is, Atlantic climate, with only short dry seasons. Parent material makeup is the main factor in inducing humification and pedogenesis:

- **Siliceous rock**: In these materials, hydroxides bound to clay lead to insolubilization and limited maturation of humic compounds. The brown humic acids and varying amount of biomolecules which are formed induce formation of aggregates which are generally unstable. The turnover of this "binding cement" is rapid. This process is termed "brunification" by Ugolini (1986) and Schlichting (1986).

- **Volcanic ashy material**: Amorphous aluminum hydroxide (with smaller amounts of iron hydroxide) plays a major part in the extremely fast insolubilization of soluble organic compounds and prevents their biodegradation (Hetier et al., 1974). With the low turnover of organic matter, this material accumulates in the soil profile and brings about andosolization. When alternate wet and dry seasons occur, as in southern Japan, maturation is followed by normal melanization. Several authors using new American soil taxonomy call this type of soil "melanudand" (Drijber and Low, 1990; Yonebashi and Hattori, 1990; Dahlgren and Ugolini, 1991; Parfitt and Clayden, 1991).

- **Fragmented limestone**, which loses a large amount of soluble calcium, causes calcic melanization of humic rendzina. Humification is then checked in its early phase and many plant residues are protected against mineralization and remain in the profile. Biomolecules are abundant due to high biological activity. Calcium favors a strong bond of organomineral complexes to clay so that both microaggregates and macroaggregates are formed. Where the climate is more variable, as in the mountains (Gaiffe, 1987), melanization is further increased, creating black humo-calcic soils.

(3) Continental climate, characterized by long dry seasons and steppe-forest vegetation. Chernozems, which show some of the same characteristics as humo-calcic soils, are saturated by calcium and are predominantly gray (black) HA. However, they have quite a few essential differences with humo-calcic soils: humification is much more developed, turnover is slower, and MRT is much higher. The FA/HA ratio is also much lower and the plant residues have almost entirely disappeared. Chernozems are the most developed humus form in soils found in temperate climates.

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